THE EFFECT OF PRESSURE AND SOLVENT QUALITY ON FIRST STAGE COAL LIQUEFACTION WITH DISPERSED CATALYSTS

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Introduction

Dispersed catalysts, both molybdenum and iron based, have been shown to be effective for coal liquefaction.[1] Most studies have tested the effectiveness of these catalysts at moderate to high hydrogen pressures, on the order of 1500 to 2500 psig (10.3 to 17.2 MPa). Coal liquefaction at lower pressures is well known. Hydrogen donor solvents, such as tetralin and dihydrophenanthrene, are capable of transferring hydrogen to the coal at low pressures, less than 400 psig (2.8 MPa).[2]

This study is aimed at exploiting a combination of dispersed catalyst activity with donor solvent quality to reduce the overall pressure of first stage coal liquefaction. Two questions are being addressed in this study. The first is how effective are dispersed catalysts for hydrogenation at lower pressures and the second is to what extent are dispersed catalysts capable of catalyzing the transfer of hydrogen to the coal. This paper presents preliminary studies aimed at addressing these two questions with model coal liquefaction solvents PANASOL (non-hydrogen donor) and tetralin (hydrogen donor).

Experimental

Feed Coal. Experiments were conducted with Blind Canyon bituminous coal (DECS-6, from the DOE/Penn State Coal Sample Bank). This coal was selected because of its low pyritic sulfur content. An analysis of the coal was presented earlier.[1]

Catalyst. A high surface area MoS_2 catalyst was used. The catalyst preparation was discussed previously.[1] The MoS_2 was prepared by reduction of ammonium heptamolybdate under H_2/H_2S in the 1-L semi-batch autoclave at 2,500 psig (17.2 MPa), 4 SCFH (0.11 Nm^3/h) of $H_2/3\%H_2S$, 425°C, and 0.5 h.. The catalyst has a BET surface area of 261 m^2/g, and elemental composition of 30% Mo, 20 % S, and 50% C.

Liquefaction Studies. Experiments were conducted by adding 3.3 g coal to a 40-mL tubular microautoclave reactor with 6.6 g of a mixture of PANASOL (obtained from Crowley Chemical) and tetralin. In experiments in which catalysts were used, 1000 ppm of Mo was added as high surface area MoS_2. The reactor was charged with the desired pressure of hydrogen and sealed. The pressurized reactor was then rapidly (1-2 minutes) heated to the liquefaction temperature (425°C) in a fluidized sandbath. Following the liquefaction period (0.5 h), the reactor was cooled and depressurized. Coal conversion was calculated from the solubility of the coal-derived products in tetrahydrofuran (THF) and in heptane as determined by a pressure filtration technique.[3] One experiment was conducted in a 1-L flow-through reactor to hydrogenate PANASOL. The conditions used in this reactor were 400 g PANASOL, 1000 ppm Mo as MoS_2, 2,500 psig (17.2 MPa), 4 SCFH (0.11 Nm^3/h) of $H_2/3\%H_2S$, 425°C, and 0.5 h.

Solvent Hydrogenation Studies. Experiments were conducted by adding 6.6 g of PANASOL or tetralin to a 40-mL tubular microautoclave reactor. In experiments in which catalysts were used, 1000 ppm of Mo was added as high surface area MoS_2. The reactor was charged with the desired pressure of hydrogen and sealed. The pressurized reactor was then rapidly (1-2 minutes) heated to the liquefaction temperature (425°C) in a fluidized sandbath. Following the liquefaction period (0.5 h), the reactor was cooled and depressurized. The liquid products were recovered from a THF rinse of the reactor.

Analytical characterization of the products is discussed in a separate paper submitted to this symposium.[4]

Discussion of Results

Solvent-Only System

A series of tests was made to investigate the effect of pressure on solvent hydrogenation. Hydrogenation of PANASOL in the presence of a high surface area MoS_2 catalyst was studied in the microautoclave. The extent of hydrogenation was determined by hydrogen consumption from the gas phase, elemental analysis, combined gas chromatography-mass spectrometry (GC-MS), low voltage high resolution mass spectrometry (LVHRMS), and nuclear magnetic resonance (NMR). The % hydrogenation of the solvent is defined as the mol% naphthalenes converted to their corresponding tetralins. Figure 1 shows the levels of hydrogenation determined from the various techniques as a function of pressure. Also on Figure 1 are the equilibrium conversions calculated for the naphthalene/tetralin system at 425°C from the data reported by Frye and Weitkamp[5]. The hydrogenation of PANASOL at 1000 psig (6.9 MPa) with no catalyst and the hydrogenation of PANASOL in the 1-L semi-batch reactor are also shown. As shown in Figure 1, the levels of hydrogenation observed in the microautoclave are significantly lower than the equilibrium for the naphthalene/tetralin system. However, hydrogenation was observed at pressures as low as 400 psig cold (2.8 MPa), 780 psig (5.4 MPa) at temperature. The results in Figure 1 illustrate the range of values of % hydrogenation obtained by the different analytical techniques. Finally, Figure 1 indicates that higher levels of hydrogenation are obtainable in the stirred 1-L autoclave (with gas flow) than in the batch microautoclave.

The reverse of this reaction, dehydrogenation of tetralin, was also studied in the microautoclaves. The dehydrogenation was done at different hydrogen pressures, 400 psig (2.8 MPa) and 1000 psig(6.9 MPa), with and without a high surface area MoS_2 catalyst for 0.5 h at 425°C. The yields of dehydrogenated compounds (naphthalenes) determined by gas chromatography with flame ionization detection (GC-FID) were $<1.0\%$ for 1000 psig (6.9 MPa) and no catalyst, 8.0% for 1000 psig (6.9 MPa) with MoS_2, and $<1.0\%$ for 400 psig (2.8 MPa) and no catalyst. The equilibrium distribution of naphthalene and tetralin at the higher pressure condition is (from Frye and Weitkamp) between 7.5 and 8.0 mol% naphthalene. The results indicate that significant levels of dehydrogenation were only observed with the catalyst present. The MoS_2 is quite effective for tetralin dehydrogenation and, in this case, equilibrium was reached from the tetralin side within the 0.5 h reaction time.

Effect of Coal on Solvent Hydrogenation

The effect of coal addition on the hydrogenation of PANASOL was studied in another series of microautoclave tests. The effect of adding 0 g, 0.1 g, 0.2 g, and 3.3 g of DECS-6 Blind Canyon coal on the amount of hydrogen taken up by the solvent in the presence of MoS_2 was investigated. The total amount of hydrogen consumed in these tests were 0.029, 0.026, 0.022, and 0.055 (0.052 and 0.055 in replicate tests) for 0, 0.1, 0.2, and 3.3 g coal respectively. Note that with no catalyst and no coal present, 0.006 moles of hydrogen was consumed and when 3.3 g coal and no catalyst were present, 0.025 mol was consumed. Hydrogen consumption with 0.1 g (0.026) and 0.2 g (0.022) coal was lower than when no coal was added or with 3.3 g coal. The relative rates of hydrogen consumption are also informative. In the absence of coal, total pressure fell gradually over the entire span of reaction time. In the presence of 3.3 g coal, the pressure dropped rapidly, then approached a limiting value, asymptotically less than when no coal was added. The rate of hydrogen consumption is presented in a figure in a separate paper at this symposium.[4] Product inspection in the latter case indicated that 8 mol% of methyltetralins was formed, but 30 mol% was formed in the former case.

The effect of added coal (3.3 g) on the hydrogenation of PANASOL to tetralins at different pressures was determined by LVHRMS. The results are summarized in Figure 2. Also shown on Figure 2 is the effect of pressure on the hydrogenation of PANASOL with no added coal. Considerably less hydrogenation of PANASOL was observed when coal was added.

To distinguish whether the added coal was competing with the PANASOL for catalytic sites or if coal was suppressing catalytically active sites, THF washed catalyst (plus any residual insoluble coal) from the test using 0.2 g coal was added to a separate test with just PANASOL. The rate of hydrogen consumption was very similar to the original case in which 0.2 g coal was added. Since solvent hydrogenation was diminished in the absence of added coal, it appears suppression rather than competition for active sites takes place. In a third test the catalyst was washed with THF and again added with PANASOL and 3.3 g DECS-6 coal. The overall coal conversions and rate of hydrogen consumption was the same as with fresh catalyst. This indicates that even though the activity of the catalyst for solvent hydrogenation was suppressed by the presence of coal, the catalyst remained effective for coal liquefaction and conversion. A separate paper that discusses this effect in more detail has been submitted to this session.[4]

The effect of coal on MoS_2 catalyzed dehydrogenation of tetralin was also studied. The amount of hydrogen produced was determined by gas analysis. When no coal was present during the dehydrogenation of tetralin, under 1000 psig N_2 (6.9 MPa), 0.005 mol of hydrogen was evolved with no catalyst present and 0.050 mol of hydrogen was evolved with added MoS_2. Exposing the MoS_2 to 0.2 g of coal resulted in the evolution of 0.010 mol of hydrogen. It appears that the presence of coal also suppresses the dehydrogenation activity of the MoS_2 catalyst (though more hydrogen was evolved than with no catalyst added). Tetralin dehydrogenation was studied in the presence of 3.3 g of coal under 1000 psig (6.9 MPa) N_2. With coal and no catalyst present, 0.003 mol of hydrogen was produced. With added MoS_2 in the presence of coal, 0.013 mol of hydrogen was produced (about 4.3 times the amount produced with no catalyst). However, coal conversion to THF and heptane soluble products was similar for the two cases.

Effect of Pressure and Solvent Quality on Coal Conversion

The effect of varying the cold pressure from 200 to 1000 psig (1.4 to 6.9 MPa) on coal conversion with added MoS_2 catalyst was investigated. The conversion of coal to THF and heptane soluble product is shown in Figure 3. The results show that coal conversion is affected by pressure; however, higher conversions are observed at 400 psig cold (2.8 MPa) with catalyst than at 1000 psig cold (6.9 MPa) without catalyst. This indicates that the catalyst is effective even at pressures as low as 400 psig cold (2.8 MPa). Figure 4 presents the effect of pressure on C_1-C_4 gas produced. As shown in Figure 4, higher amounts of gas were produced with increasing pressure (also increasing conversion).

The effect of solvent quality on coal conversion with no added catalyst was investigated by varying the ratio of tetralin to PANASOL. These results are shown on Figure 5. Also shown in this Figure are the earlier results using added catalyst with 100% PANASOL at different pressures. In order to compare the magnitude of the catalytic (100% PANASOL) with the hydrogen donor (varying tetralin to PANASOL ratios) effect, a common basis was selected in the following way. The positioning of the catalytic data (obtained at different pressures with 100% PANASOL) with respect to the x-axis was determined based on the observed amounts of tetralins produced from PANASOL as a function of pressure in tests with no coal added (from Figure 1). Thus, these estimates represent the maximum expected concentration of tetralins in the PANASOL/coal/catalyst system that could be achieved by the end of the 0.5 h span of reaction. Using this as a basis, higher conversions of coal to soluble products are observed with added catalyst than with tetralin/PANASOL mixtures. The differences become smaller as maximum THF conversion is approached in both systems.

Effect of Catalyst Addition on Mixed Donor/Non-Donor Systems

In non-catalytic experiments at 400 psig H_2 (2.8 MPa), hydrogen was transferred to the coal from the dehydrogenation of tetralin. With a mixture of 25% tetralin with 75% PANASOL as the solvent for DECS-6 coal, the hydrogen transferred to the coal was calculated based on the amount of tetralin converted to naphthalene (by LVHRMS) and the detected hydrogen in the gas phase. The calculated amount of hydrogen transferred to the coal was 0.011 mol (the total hydrogen produced from the tetralin was 0.015 mol). This level of hydrogen transferred was equivalent to the hydrogen transferred from the gas phase in catalytic cases with a non-donor at 300-400 psig H_2 cold (2 to 2.8 MPa).

MoS_2 was added to a system containing a mixture of 20% tetralin and 80% PANASOL as the solvent for DECS-6 coal at 400 psig H_2 cold (2.8 MPa). Dehydrogenation of the tetralin produced 0.038 mol of hydrogen, and 0.024 mol of hydrogen were transferred to coal. Approximately 2.5 times the amount of hydrogen was produced from the tetralin than in the non-catalytic case, and 2.0 times the amount of hydrogen was transferred to the coal than in the non-catalytic case. It is not clear whether the additional hydrogen was transferred to the coal by direct catalytic hydrogen transfer or catalytic dehydrogenation to the gas phase followed by catalytic hydrogenation of the coal. Note that the addition of catalyst to the mixed hydrogen donor/non-donor system resulted in higher coal conversion to THF soluble product than in the non-catalytic system (80% with a catalyst compared to 68% without a catalyst).

Conclusions and Future Efforts

The major results from this effort can be summarized as:

1) Catalyst activity for coal conversion is observed at pressures as low as 400 psig (2.8 MPa).

2) MoS_2 catalysts can act as effective dehydrogenation catalysts even under hydrogen pressures, therefore these catalysts may be effective for transferring hydrogen from solvents to coal.

3) Production of C_1-C_4 gases increases with increasing hydrogen pressure.

4) While coal can inhibit the activity of MoS_2 catalysts for solvent hydrogenation, the activity of these catalysts for coal conversion remains high after several passes in a coal liquefaction environment.

Future tests are planned to investigate the interrelationship of solvent quality, pressure, and catalyst activity in an effort to reduce the overall pressure used in coal liquefaction. Based on the results obtained thus far, an appropriate combination of solvent quality and catalyst activity may allow significant reductions in the overall pressure of first stage coal liquefaction.

Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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Figure 1. Effect of Reactor Pressure on PANASOL Hydrogenation in a Microautoclave at 425 °C with 1000 ppm Mo

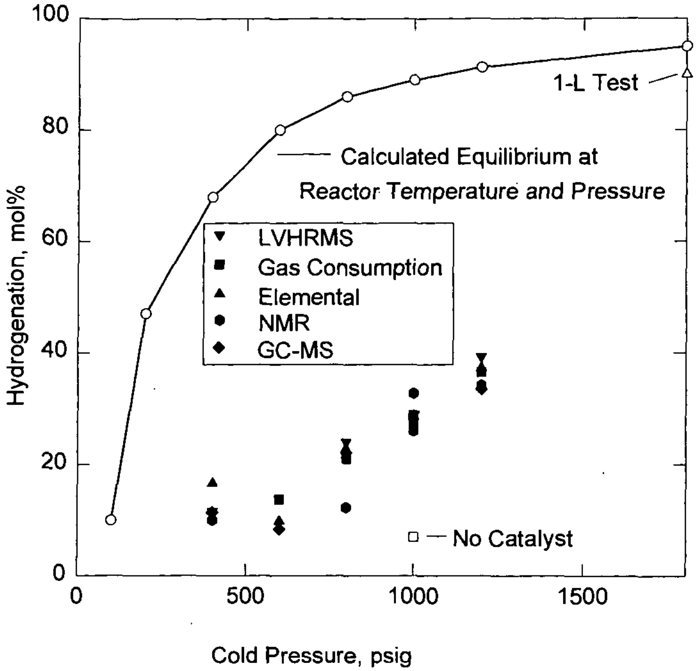


Figure 2. Effect of Pressure on %Tetralins in Total Product from a Microautoclave at 425 °C with 1000 ppm Mo

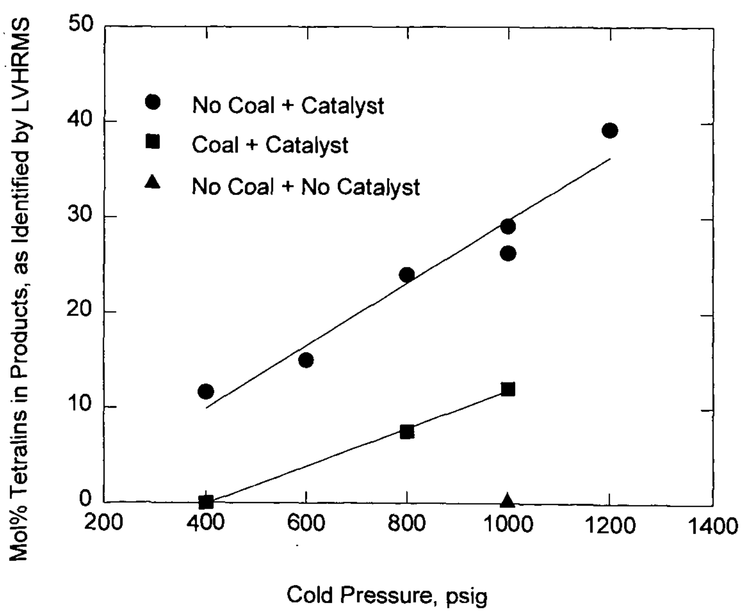


Figure 3. Effect of Pressure on DECS-6 Coal Conversion with PANASOL in a Microautoclave at 425 °C with 1000 ppm Mo

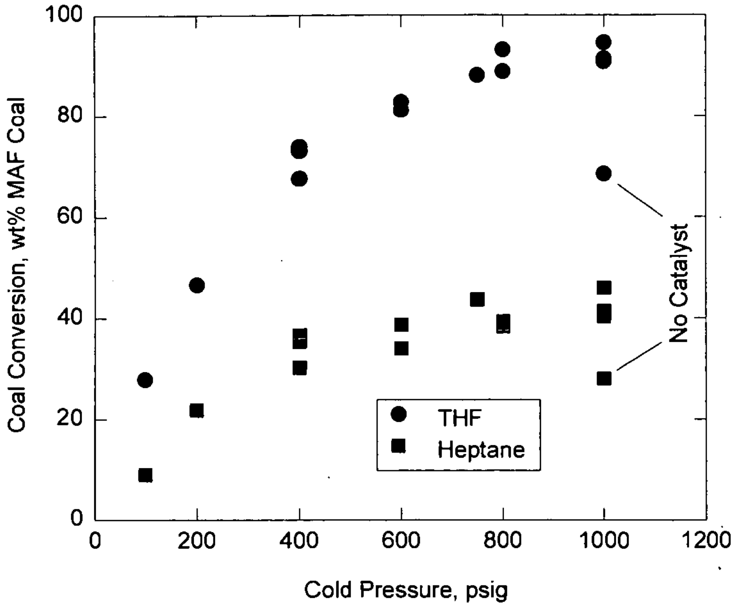


Figure 4. Effect of Pressure on C_1-C_4 Produced in Microautoclave at 425 °C with 1000 ppm Mo using DECS-6 and PANASOL

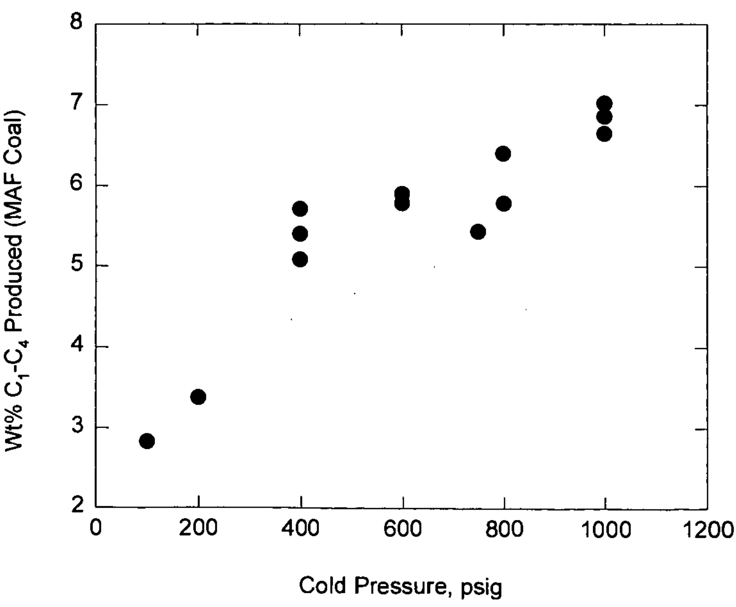
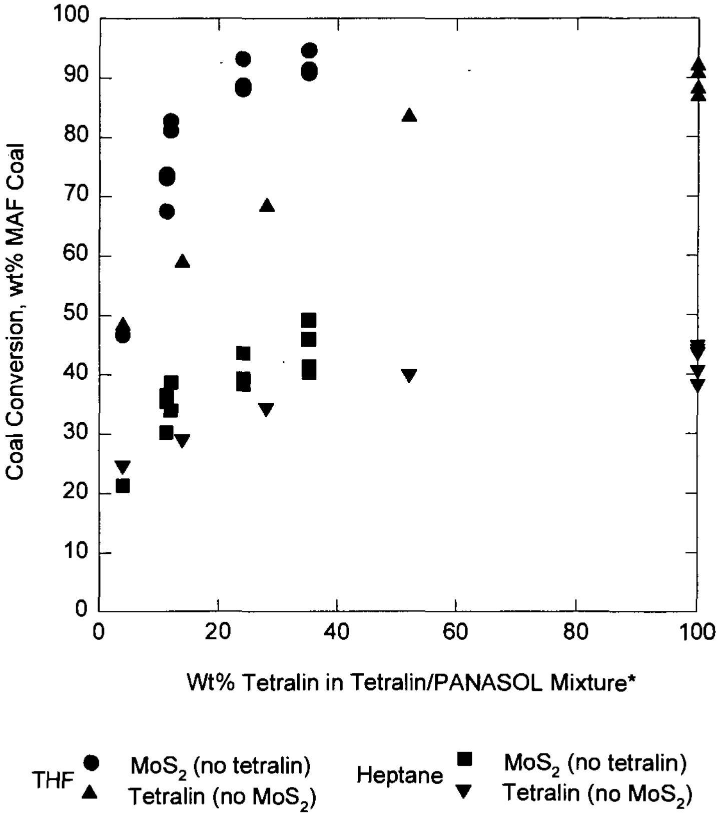


Figure 5. Comparison of coal conversions in mixtures of tetralin/PANASOL with no catalyst to 100% PANASOL (at different pressures) with a catalyst.



* Calculated for Catalytic System